



TiO₂/graphene-based nanocomposites for water treatment: A brief overview of charge carrier transfer, antimicrobial and photocatalytic performance

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ABSTRACT

This brief review presents the principal results of studies on the photocatalytic and antimicrobial activity of TiO₂/graphene nanohybrid materials with an application for water and wastewater treatment. The impact of different kind of graphene materials on the photoactivity of new hybrid photocatalysts was discussed in detail. It was generally concluded that graphene matrix acts as an acceptor and transporter of electrons photogenerated during TiO₂ excitation. Mentioned charge carriers can be freely transferred through the graphene sheets reducing the fast $e^- - h^+$ recombination, thus enhancing the photocatalytic performance of TiO₂-graphene systems. Additionally, theoretically negatively charged and high surface area of graphene flakes benefits the enhancement of an adsorption rate of pollutants contained in water (especially cationic dyes like methylene blue). Formation of chemical interactions between d orbital in TiO₂ and π orbital in graphene impacts on the narrowing of the band-gap of new hybrid nanocomposites, hence the significant enhancement of photocatalytic activity in the visible region. The occurrence of chemical bonds strongly depends on the type of fabrication method, conditions of preparation, as well as the presence of different functional groups on graphene matrix that greatly facilitates the formation of d– π interactions. The higher amount of reactive oxygen species, especially hydroxyl radicals mainly responsible for the effective oxidation of organic compounds, increases the photocatalytic decomposition rate of degraded pollutants. The effectiveness of $\cdot OH$ formation in TiO₂/graphene systems could be also attributed to the use of titania nanoparticles with exposed {001} active facets.

1. Introduction

Over the past decade, a large number of scientific papers related to the preparation, characterization and application of a new type of hybrid nanocomposites based on titanium dioxide and graphene materials, have been intensively published. It is noteworthy that for many years before graphene was extracted from graphite flake [1,2], a large number of studies on TiO₂ modifications using various carbon materials were successfully carried out [3–7]. In almost every article on photocatalysis with the application of titanium dioxide, information on the large band-gap of titania resulting in limiting the use of solar energy for excitation of TiO₂ can be easily found. Moreover, fast recombination of photoexcited charge carriers results in a relatively low photocatalytic efficiency of pristine TiO₂ [8]. Thus, many of these papers present the results of research on the metal ions or non-metals modifications of starting materials or coupling of TiO₂ with other semiconductors, especially to obtain visible-light-driven photocatalysts with enhanced photoactivity and suppressed charge carriers recombination [9,10].

Modification of titanium dioxide with various carbon materials is one of the most frequently described among other processes due to the possibility of using a large number of easily accessible and low-cost carbon precursors. High surface area, structural changes observable on the surface or in the bulk of TiO₂: presence of additional energy states as a result of carbon incorporation into titania lattice, increased number of active sites on modified surface as well as formation of oxygen vacancies and Ti³⁺ species contributes a significant increase of the photocatalytic activity [4,11]. Moreover, carbon-doping of TiO₂ is particularly aimed at improving the photocatalytic activity of the obtained photocatalysts as a result of strong absorption of light in the range of visible light due to band gap narrowing [7]. However, it should be noted that the effectiveness of the photocatalytic oxidation of water pollutants strongly depends on the position of carbon dopant in TiO₂ lattice. Ratova et al. [8] proved that partial substitution of Ti with carbon atoms by means of reactive pulse DC magnetron co-sputtering leads to obtaining visible-light-driven carbon-doped TiO₂ photocatalysts by producing of hybrid orbital just below the titania

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conduction band. Thereby, the presence of the additional energy orbital prevents fast recombination of photogenerated charge carriers [12]. However, it should be stated that conducting effective carbon-doping of titanium dioxide is rather difficult to implement and depends on a number of factors that should be strictly adhered.

Recently, the combination of TiO₂ with graphene attracts considerable interest in the field of the preparation of novel nanohybrid materials that benefits effective separation of photoexcited electron-hole charge carriers, thus enhancing the photocatalytic performance of these composites. Unique properties of graphene (flexible structure with the theoretically high surface area as well as excellent thermal, mechanical, optical and electrical properties) [13–15] make it highly attractive in comparison to other carbon-incorporated TiO₂ nanomaterials. Additionally, graphene nanomaterials are well known as anti-fouling agents, sorbents of sodium cations in the desalination process and modified with hydrogen and/or nitrogen facilitate the selective passage of either anions or cations [16]. The superiority of graphene to traditional materials is mainly due to its unique electrical, mechanical, optical and thermal properties. However, the properties of the TiO₂/graphene-based nanocomposites are determined by the type of graphene material used in the preparation process. 2D-graphene is composed of a single (an ideal sheet) to less than ten planar sheets of carbon atoms with sp² hybridization. According to Pei [17], the graphene oxide sheets consist mainly of sp²- and partially of sp³-hybridized carbon atoms, with covalently-bonded oxygen-containing functional groups combined with non-oxidized parts of the sheet. The atomic structure of GO is highly disordered compared to the pristine graphene. Since GO functions as an electrical insulator due to the disturbance of its sp² bonding networks, the application of GO in composite materials is limited. By reducing GO, the removal of oxidized part of GO sheets occurs. This process leads to the formation of the reduced GO forms with excellent electrical conductivity and rapid electron transfer, similar to that of pristine graphene [18]. Combination of rGO and semiconductor nanoparticles causes the formation of a hybrid system with suppressed recombination of charge carriers in the semiconductor due to the transfer of electrons through rGO sheets.

The first theoretical calculations on a graphene sheet modified with titanium for hydrogen storage were published in 2007 [19]. It was found that under air conditions, graphene decoration with titanium atoms strongly enhances the capacity of hydrogen storage. In 2008, Williams et al. [20] were the first to propose a new method of UV-assisted photocatalytic reduction of graphene oxide using TiO₂, thus obtaining active nanocomposites. It is well known that exfoliated graphene sheets show a high tendency to aggregate in solution as a result of the strong van der Waals interactions between separated single layers. Direct interactions between graphene and titania nanoparticles suppress the re-aggregation of exfoliated GO sheets and secondly lead to obtaining well-separated reduced graphene oxide sheets decorated with TiO₂. This phenomenon was also confirmed by Akhavan and Ghaderi [21]. It was found that post-annealing of the TiO₂/graphene oxide thin films at 400 °C in air resulted in the partial formation of a Ti–C bond between the TiO₂ and graphene sheets. The occurrence of this type of bonds, as well as the improvement of interfacial contact through homogeneous distribution of titania nanoparticles on the graphene sheets without chemical bonding, benefits the effective transfer of photogenerated electrons from conduction band of TiO₂ to electronic state of graphene suppressing recombination of e[−]–h⁺ charge carriers in titania [22,23], thus significantly improving the efficiency of the photocatalytic oxidation of contaminants. Moreover, a high surface area of graphene sheets hence improved adsorption abilities, and photocatalytic properties of TiO₂ make these nanohybrids attractive for water and wastewater treatment.

In this review, we try to briefly discuss the role of graphene-based materials (graphene oxide or reduced graphene oxide) on the photocatalytic activity of TiO₂/graphene nanohybrids with an application for the efficient decomposition of hazardous compounds from water and

wastewater. The mechanisms of the degradation of various water pollutants are also tried to explain.

2. Photocatalytic oxidation of pollutants in the presence of TiO₂/graphene nanohybrids

The first published papers on TiO₂-graphene composites directly concerned the preparation methods and detailed characteristics of obtained nanohybrids [20,24,25]. In 2008 Akhavan and Ghaderi [21] published an article on the UV-assisted reduction of graphene oxide in the presence of TiO₂ caused obtaining of hybrid nanocomposites with an enhanced photocatalytic activity that was tested against *E. coli* bacteria inactivation under solar light irradiation. In 2010 Zhang et al. [26] presented one of the first studies on the application of TiO₂-graphene materials as photocatalysts for the decomposition of contaminants from water. New photocatalytic systems are commonly tested on the basis of photodegradation of different organic pollutants contained in water and wastewater.

2.1. Dyes photodecomposition

Removal of anionic or cationic (especially methylene blue, MB) dyes is the most frequently reported results describing the photocatalytic effectiveness of TiO₂-graphene nanocomposites. In Table 1 the representative summary of the photodegradation of various types of dyes in the presence of TiO₂-graphene materials is presented. Table 1

Zhang et al. [26] reported the enhanced photocatalytic activity of TiO₂-graphene oxide photocatalysts prepared with the use of commercial P25 and GO synthesized by the modified Hummers' method. It was found that hydrothermally prepared nanocomposites possessed enhanced adsorptivity of methylene blue (cationic dye) due to the negatively charged surface of the GO matrix, narrowed band-gap that strongly improve the photocatalytic activity under visible light and enhanced charge carriers separation making the composites chemically stable. The formation of chemical bonds between TiO₂ and GO additionally benefits the high photocatalytic removal rate of MB dye under UV light. These findings were also been confirmed by others [27,28].

Zhou et al. [29] attributed the increase of photodegradation rate of MB to the single-layer structure of graphene, homogeneous distribution of TiO₂ nanoparticles through graphene matrix, chemical bonding of TiO₂-GO (formation of Ti–C bonds) causing the band-gap red-shift, effective transport of photoexcited electrons to lower Fermi level of GO sheet (confirmed by means of photoluminescence study), as well as the amount of used GO powder. The optimal amount of GO that promotes the increase of photoactivity was also discussed. An overhigh concentration of GO reduces the light absorption by TiO₂ resulting in a decrease of photoactivity. Similar conclusions were also been found by Wang et al. [30]. In addition, it was also stated that the photocatalytic performance of TiO₂-graphene nanocomposites strongly depends on the type of prepared titania and application of high-energy anatase TiO₂ {001} facets significantly increases the decomposition rate of MB dye. Secondly, preparation of TiO₂-graphene materials with exposed {001} facets causes the formation of a higher amount of hydroxyl radicals that improves the photocatalytic performance, indicating high chemical stability (proved on the basis of multi-cycle photoactivity tests). The mechanism of MB photooxidation mainly by means of photogenerated hydroxyl radicals was also discussed by Zhao et al. [31]. However, the proposed mechanism was carefully verified and corrected according to Nosaka et al. [32] and Rincón et al. [33]. In the aqueous systems, superoxide radicals are transformed rapidly to H₂O₂. During the photocatalytic (or photolytic) reaction of hydrogen peroxide, the generation of ·OH radicals is observed. The formation of ·OH radicals could be presented as follows (Eqs. (1)–(8)):

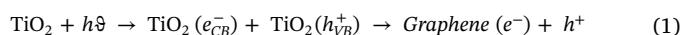
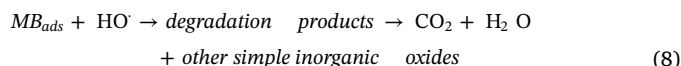
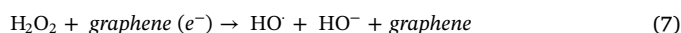
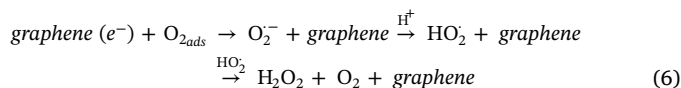
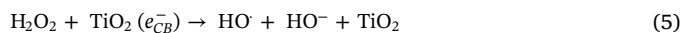
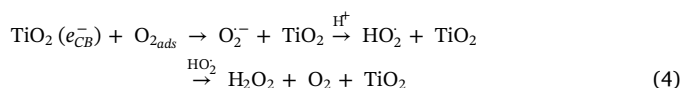
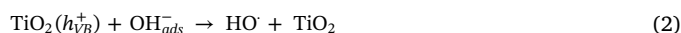


Table 1
Summary information of various dyes pollutants photooxidation by TiO₂-graphene nanohybrids.

Type of pollutant	Type of material	Light source	Properties	Ref.
Methylene blue	TiO ₂ /GO	UV, visible light	enhanced GO adsorptivity, band-gap narrowing, charge carriers separation	[26]
Methylene blue	TiO ₂ /rGO	visible light (> 400 nm)	band-gap narrowing, charge carriers separation, enhanced GO adsorptivity	[28]
Methylene blue	TiO ₂ /GO, TiO ₂ /rGO	simulated solar light	homogeneous distribution of TiO ₂ , graphene single-layer structure, charge carriers separation	[29]
Methylene blue	TiO ₂ /GO, TiO ₂ /rGO	visible light (> 400 nm)	presence of (001) anatase reactive facets, effective charge carriers separation, hydroxyl radicals formation	[30]
Methylene blue	TiO ₂ /rGO (thermal reduction)	visible light (> 450 nm, > 600 nm, > 700 nm)	hindered recombination, enhanced amount of ·OH, high concentration of active sites on graphene surface	[31]
Methylene blue	TiO ₂ /GO, TiO ₂ /rGO	UV, visible light	enhanced GO adsorptivity, the optimal amount of GO, charge carriers separation, large surface area	[34]
Methylene blue	TiO ₂ P25/GO, TiO ₂ P25/rGO	UV (max. 365 nm)	band-gap narrowing, enhanced GO adsorptivity, improved but quite low charge carriers separation	[35]
Methylene blue, methyl orange	TiO ₂ microspheres/rGO	UV-visible light (max. 365 nm)	significant enhancing of adsorption capacity, changes in surface area and pore size of TiO ₂ /rGO	[36]
Methylene blue, methyl orange	TiO ₂ /GO, TiO ₂ /rGO	TiO ₂ P25/GO	GO/rGO enhanced adsorptivity of cationic dye, charge carriers separation	[37]
Methyl orange	TiO ₂ /GO	UV-visible light (main 365 nm)	band-gap narrowing, crystallites growth due to calcination, ROS formation	[38]
Methyl orange	TiO ₂ /GO and TiO ₂ /rGO	UV, visible light	calcination favours oxidation of residual organics in the rGO-TiO ₂ and better crystallization of TiO ₂ NPS with smaller diameters	[39]
Methyl orange	TiO ₂ nanofibers/rGO	UV	charge carrier suppression due to the interface of TiO ₂ and rGO	[40]
Methyl orange	TiO ₂ /rGO	Visible light	enhanced adsorption of MO due to the larger surface area, red-shift of absorption edge	[41]
Rhodamine B	TiO ₂ /rGO	UV-C, visible light	effective ROS formation (·O ₂ H as main ROS), hindered recombination, faster electron transfer	[42]
Rhodamine B	TiO ₂ /rGO	Visible light	charge carrier suppression, red-shift of absorption edge	[43]
Rhodamine B	TNT/rGO	UV-Vis light	enhanced adsorption capacity	[44]
Rhodamine B	TiO ₂ /rGO	Visible light	effective separation of charge carriers, harvesting under visible light	[45]
Rhodamine B	TiO ₂ /rGO	UV	excellent electron trapping and transportation properties of TiO ₂ /rGO	[46]



Formation of chemical bonds between TiO₂ and graphene (d- π interactions) favours effective photogenerated electron transfer from conduction band (d orbital) of titania to Fermi level (π orbital) of the graphene sheet. The TiO₂(e_{CB}⁻) could be freely transported through the graphene matrix that acts as an acceptor of excited electrons and finally transferred to the surface to react with water and dissolved oxygen forming different types of reactive oxygen species ROS (hydroxyl radicals with high oxidation potential as well as superoxide radicals) that can effectively oxidize water organic pollutants.

The enhanced adsorptivity of GO and rGO sheets in relation to cationic has been confirmed i.a. by Nguyen et al. [36] and Atchudan et al. [37]. The adsorption abilities of prepared TiO₂-GO/rGO nanocomposites were studied on the basis of adsorption of cationic methylene blue (MB) and anionic methyl orange (MO) dyes. It was found that negatively charged GO/rGO sheets benefit cationic MB sorption in comparison to anionic MO. In both cases, the photooxidation process was much faster for MB dye than for MO.

The schema of the detailed mechanism of photocatalytic oxidation of Rhodamine B (RhB) from water (shown in Fig. 1) in the presence of TiO₂-graphene nanohybrids was explained by Byzyski et al. [42]. It was noted that TiO₂ nanoparticles homogeneously dispersed around the reduced graphene oxide structure inhibit the charge carriers recombination. Different dominant reactive oxygen species were responsible for discolouration of RhB dye in the presence of obtained heterostructure (oxygen vacancy for UV irradiation and ·O₂H radical for visible light).

2.2. Phenol photooxidation

Phenols are considered to be one of the important organic pollutants discharged into the environment. Phenols are considered as primary pollutants since they are harmful to organisms even at low concentration. It is also worth noting that phenol has been commonly used as a popular non-visible absorbing target to study the photocatalytic performance of TiO₂-based nanomaterials [47,48]. Kim et al. [49] tested the photocatalytic activity of titanate nanotubes-rGO nanocomposites on the basis of phenol removal under visible light. The 3.8 higher photocatalytic performance of phenol decomposition was attributed to the synergistic effect of rGO and TNT. The successful suppression of charge carriers recombination of TNT-rGO nanohybrids was confirmed on the basis of photoluminescence studies. Moreover, the enhancement of the photoactivity in the visible region was attributed to the band-gap narrowing due to rGO doping on TNT and relatively large surface area of TNT-rGO materials providing a greater amount of active sites, thus forming the higher amount of hydroxyl radicals. It was generally concluded that phenol photodegradation was primarily induced by ·OH radicals. Similar findings were also discussed by Iqbal et al. [50]. Additionally, the mesoporous structure of TiO₂-rGO photocatalysts and the impact of rGO amount in nanomaterials on the photocatalytic

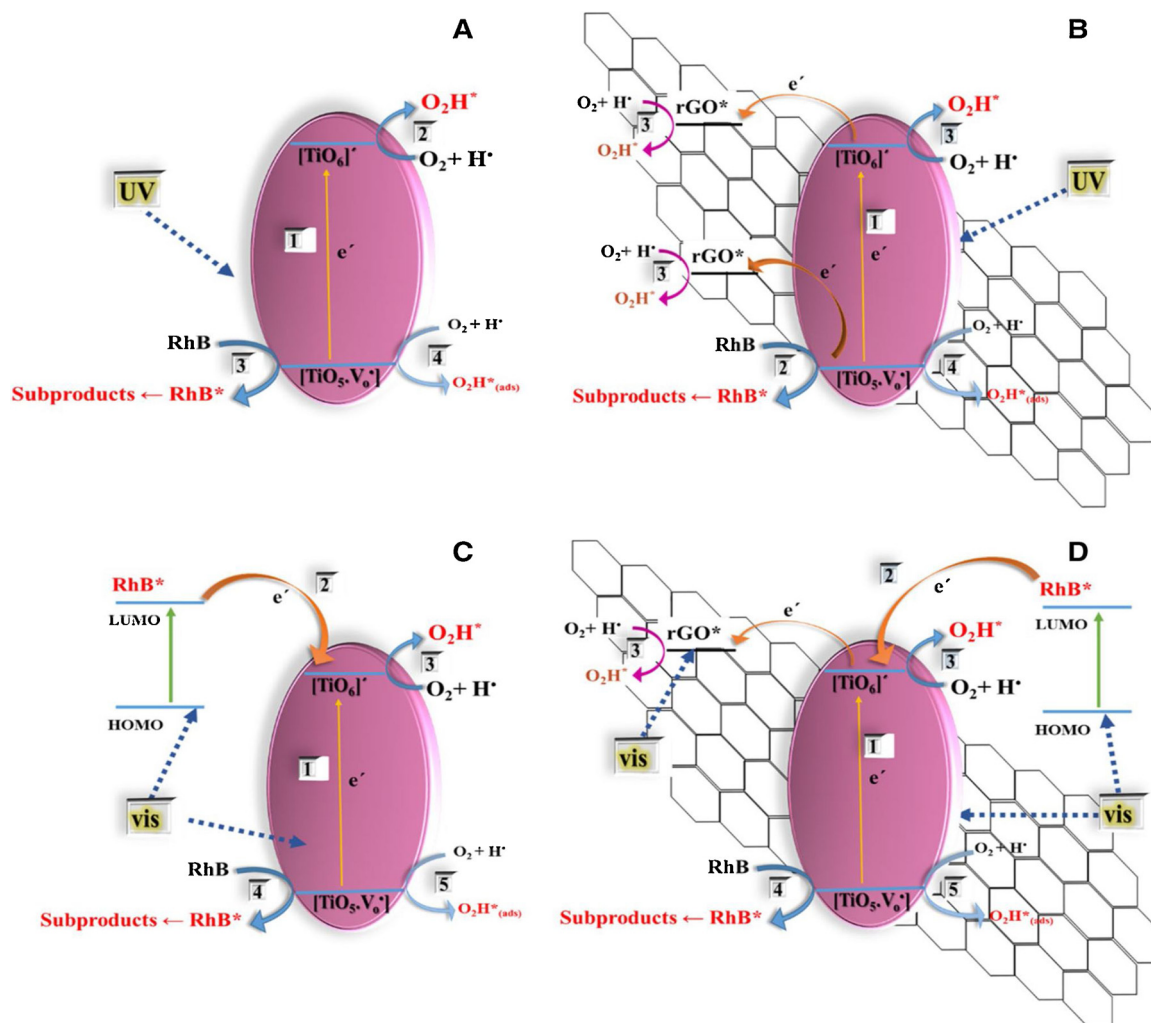


Fig. 1. Scheme of proposed RhB discoloration for TiO₂ under a) UV and c) visible illumination and for TiO₂-rGO under b) UV and d) visible illumination. The numbers indicated the sequence which steps mechanism occurs [35] [42, RSC advances by RSC Publishing. Reproduced with permission of RSC Publishing in the format Journal/magazine via Copyright Clearance Center].

performance were mentioned.

Contrary to Iqbal et al. [50], Minella et al. [51] reported that the phenol photodegradation rate did not increase with the increase of rGO in nanocomposites. In this case, the greater amount of rGO hindered the substrate transformation. Very low adsorption and decomposition rates of phenol were found for both UV-VIS and visible light experiments. Two possible explanations were given: (i) the rGO matrix is not able to trap the electrons from TiO₂ conduction band and the recombination occurs as fast as in typical titania nanoparticles or (ii) the HOMO of phenol is lower than energy state of rGO sheet with photogenerated electron vacancies. Fu et al. [52] reported enhanced adsorption of phenol on TiO₂-graphene nanocomposites. The increase of phenol adsorption rate was related to the homogeneous distribution of nanosized titania particles on the GO sheets.

2.3. Photoremoval of other organic compounds from water

The photocatalytic oxidation processes of dyes and phenolic compounds as model water pollutants are the most widely studied in the presence of TiO₂/graphene-based nanocomposites. However, different groups of pharmaceuticals as hazardous water contaminants have been also decomposed using TiO₂/graphene hybrids. Pastrana-Martínez et al. [53] prepared TiO₂/rGO nanomaterials on the basis of liquid phase deposition followed by post-thermal reduction at 200 or 350 °C. The

photocatalytic efficiency under near-UV-vis and visible light irradiation was calculated based on diphenhydramine pharmaceutical removal. It was generally concluded that the photocatalytic activity significantly depended on post-calcination temperature and GO content. The GO sheets upon binding with TiO₂ act as an electron acceptor or electron donor under UV and visible light excitation, respectively. Bhatia et al. [54] decomposed atenolol under visible light in the presence of TiO₂/rGO nanocomposites. The incorporation of hydrothermally reduced graphene in TiO₂ facilitated more adsorption sites and hindered the recombination of electron-hole pairs. The visible-light activity of prepared composites was due to the red-shift of the absorption edge. In contrary, Lin et al. [55] found that TiO₂/rGO photocatalysts were much more active under UV light than under visible. The efficiency of the photooxidation of ibuprofen, carbamazepine and sulfamethoxazole pharmaceuticals was related with a reduced recombination rate of photoexcited charge carriers. TiO₂@rGO nanocomposite efficiently activated with UVA/LED and H₂O₂ were also tested for acetaminophen photodecomposition and mineralization [56]. It was found that the rGO content (optimal for 3 wt.% of rGO) strongly increased photocatalytic activity.

2.4. Chapter summary

On the basis of the studies on the photocatalytic degradation of

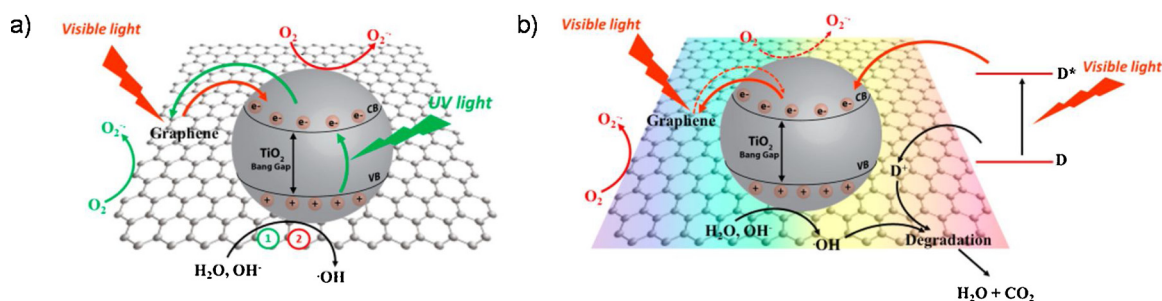


Fig. 2. Diagrams of a) the mechanisms of UV and visible light activation of TiO₂ with graphene, b) the mechanisms of UV and visible light activation of TiO₂ with graphene in the presence of dye (D) [57, Reproduced with permission from R. Giovannetti, Catalysts; published by MDPI, 2017].

various groups of organic pollutants contaminated water in the presence of TiO₂/graphene hybrids (with formed Ti–C bonds), it was generally concluded that the role of graphene matrix as photogenerated electrons acceptor is crucial in the suppression of charge carriers recombination of photocatalyst nanoparticles resulting in increased effectiveness of the water treatment. The role of enhanced cationic dye adsorption abilities of new nanocomposites was related to the negatively charged surface of graphene sheets were also strongly highlighted. Additionally, the utilization of high-energy anatase TiO₂ {001} facets causes the formation of a higher amount of hydroxyl radicals responsible for the effective oxidation of water compounds. The mechanisms of photoexcitation of TiO₂/graphene hybrids under UV and visible light that can sum up this section were presented in Fig. 2 [57].

3. Photoinactivation of pathogen cells

Structure morphology and composition, nanoscale size distribution, high surface to volume ratio as well as other significant physicochemical properties of different metal-oxide semiconductors were demonstrated to be essential for disinfection [58]. The main role of the graphene matrix in the photocatalytic inactivation of various pathogen cells is similar to this proposed for photocatalytic oxidation of organic compounds in water and wastewater. Graphene sheets, especially reduced form, decorated with TiO₂ nanoparticles act as photogenerated electrons acceptor and transporter, successfully suppress the recombination of the photoexcited pairs, thus increasing the quantum efficiency of the microbial inactivation process. Exemplary deactivation processes of selected types of microorganisms in the presence of graphene decorated pristine or modified TiO₂ are presented in Table 2.

Akhavan and Ghaderi [21] found that the high-performance graphene/TiO₂ thin film nanocomposites could be effectively utilized against *Escherichia coli* bacteria inactivation in an aqueous solution under solar light irradiation. It was concluded that the enhanced photocatalytic inactivation of *E. coli* cells was possible due to the presence of highly reduced graphene oxide platelets obtained on the UV-assisted reduction of graphene oxide in the presence of TiO₂. It is noteworthy that the *E. coli* inactivation process strongly related to the reduction rate of graphene oxide causing the accumulation of photoexcited electrons on the surface of the TiO₂ thin film, thus highly enhances the visible-light-induced antibacterial activity.

Cao et al. [59] firstly tested the antimicrobial activity of ultrafine TiO₂/graphene nanocomposites under indoor natural light irradiation. The red-shift of the absorption edge attributed to the presence of Ti–C bonds in the TiO₂/graphene matrix was found for prepared samples. The formation of Ti–C bonds was possible due to the direct redox reaction of TiCl₃ in acidic medium and graphene oxide dispersion. The Ti³⁺ cations led to an effective reduction of graphene oxide that surface is covered with negatively charged (in aqueous solution) epoxy, hydroxyl and carboxylic groups what is beneficial for interacting with Ti³⁺ cations [60]. The titanium ions were simultaneously oxidized to TiO₂, confirming the formation of chemically bonded visible-active

TiO₂/graphene nanocomposites. The extended light absorption range, efficient separation of photogenerated charge carriers, thereby formation of a higher amount of ROS and optimal concentration of graphene in nanocomposite result in excellent inactivation rate of *E. coli* bacteria. Dominant impact of reactive oxygen species on photocatalytic inactivation of *E. coli* was also discussed by Wanag et al. [61].

Yin et al. [62] studied the photobiocidal capability of free-standing porous scaffolds composed of functionalized graphene (in a reduced form) honeycomb structures decorated with TiO₂ P25 nanoparticles. It was noted that the TiO₂ nanoparticles were successfully dispersed within the walls of the obtained porous composite film generally benefiting the electron transport and suppressing the recombination of photoexcited charge carriers. The fabricated TiO₂/graphene honeycomb film electrodes show excellent broad-spectrum antibacterial activity against both *Escherichia coli* and *Pseudomonas aeruginosa*.

The other strategy, commonly discussed in the literature, for increasing the photocatalytic efficiency is metal-ions or metal doping of TiO₂/graphene nanostructures, e.g. with Au [63], Ag [64]. Metal nanoparticles provide the antimicrobial ability due to its small size that causes the easier penetration, thus contributes to both membrane and antioxidant systems destruction resulting in an effective degradation of microorganisms cells.

He et al. [63] proved that the toxicity towards biological pathogens not only relies on the nature of the cell wall but strongly depends on cell membranes, cellular enzymes and biochemical events. The prepared Au-TiO₂/nanocomposite on monolayer graphene nanomaterials were more toxic to Gram-positive than to Gram-negative bacteria and fungi. The detailed discussion on energy band structure includes two types of heterojunctions: Au-TiO₂ and TiO₂/GR in the tested nanocomposite. On the basis of theoretical calculations, it was concluded that this kind of heterojunctions illustrates a space charge layers, band bending, and the formation of a Schottky barrier as it was presented in Fig. 3. When TiO₂ and Au nanoparticles are connected electrically, electron transfer from graphene and Au particles to TiO₂ until their Fermi levels align. The band bending as a result of the alignment of the Fermi level causes the reduction of the distance between conduction and valence bands, thus resulting in the red-shift of the absorption edge. In this case, the formed heterojunctions enhance the charge carrier rate, suppressing the recombination of $e_{CB}^- - h_{VB}^+$ carriers by serving as an electron trap. Then the electrons accumulated on TiO₂ surface participate in the chemical formation of reactive oxygen species accelerating the effective inactivation of *Rhodopseudomonas palustris*, *E. coli* as well as *Candida* fungus.

Liu et al. [64] proposed a two-step method of preparation of graphene oxide-TiO₂ nanorods-Ag composites with superior antibacterial activity under solar light. The TiO₂-Ag nanorods were distributed homogeneously and well anchored on the GO sheet without aggregation. The visible light response found for prepared samples was promoted by chemical bonding of GO structure and TiO₂ or TiO₂-Ag nanoparticles. However, quite a high inactivation rate of *E. coli* cells was also achieved for GO-Ag nanocomposites even without irradiation that

Table 2
Summary information of selected waterborne pathogens inactivation on TiO₂/graphene nanohybrids.

Microorganism	Type of composite	Light source	Properties	Ref.
Bacteria cells				
<i>Escherichia coli</i>	TiO ₂ /rGO from UV-assisted GO reduction	solar light	band-gap narrowing, high GO reduction rate, increased accumulation of e ⁻ on TiO ₂ surface	[21]
<i>Staphylococcus aureus</i>	TiO ₂ /GO/bacterial cellulose sheets	near UV	decrease in cell viability, effective ROS formation	[38]
<i>Escherichia coli</i>	chemically bonded TiO ₂ /rGO (sol-gel method)	indoor natural light	band-gap narrowing, chemical bonding, charge carriers separation, high amount of ROS, optimal concentration of GO	[59]
<i>Escherichia coli</i> , <i>Pseudomonas aeruginosa</i>	TiO ₂ P25/rGO electrodes	artificial solar light	charge carriers separation, improved electrochemical activity, light-harvesting efficiency	[62]
<i>Escherichia coli</i> , <i>Rhodospseudomonas palustris</i>	Au-TiO ₂ P25/rGO	solar light	band-gap narrowing, charge carriers separation, high amount of ROS	[63]
<i>Escherichia coli</i>	Ag-TiO ₂ nanorods/GO	visible light	GO chemically bonded to Ag NPs-TiO ₂ , the important role of Ag NPs concentration	[64]
<i>Escherichia coli</i>	TiO ₂ /Ag ₃ PO ₄ /GR	UV light	improved dispersibility, charge carriers separation, effective ROS formation	[65]
<i>Staphylococcus aureus</i> , <i>Enterococcus faecalis</i>	TiO ₂ /rGO, Fe ₃ N-TiO ₂ /rGO	UV light (λ = 254 nm), visible light	harmless for skin cells, good biocompatibility	[66]
<i>Campylobacter jejuni</i> , <i>Vibrio cholerae</i> , <i>Escherichia coli</i> , <i>Staphylococcus aureus</i>	Ag/TiO ₂ /rGO	UV light	reduction in bacterial growth, hydrophobicity autoaggregation, motility	[67]
Fungal cells				
<i>Candida</i>	Au-TiO ₂ P25/rGO	artificial solar light	band-gap narrowing, charge carriers separation, high amount of ROS	[63]

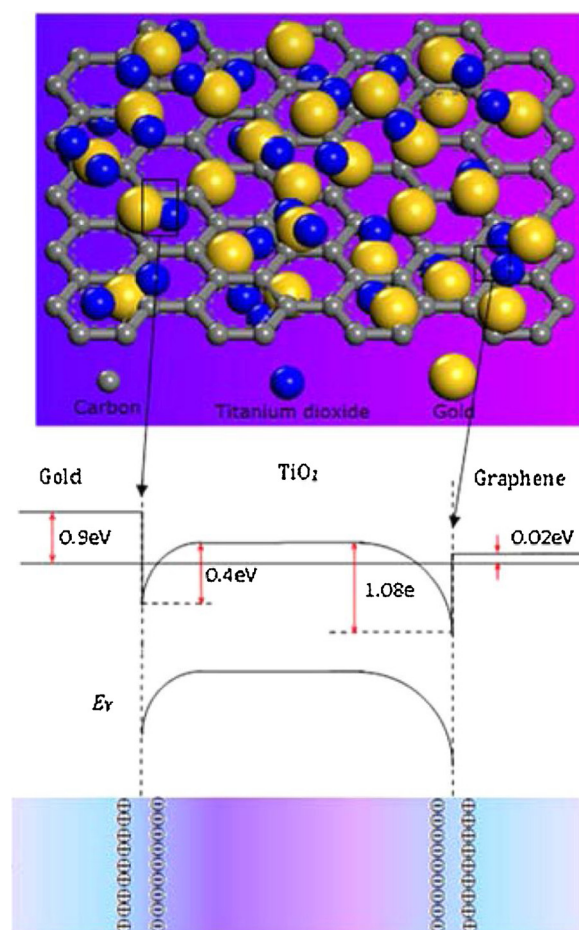


Fig. 3. Schematic for the energy band structure of the two heterojunctions (Au/TiO₂ and TiO₂/GR) in Au-TiO₂ nanocomposite on monolayer graphene [63, reproduced from: W. He, H. Huang, J. Yan, J. Zhu, Photocatalytic and antibacterial properties of Au-TiO₂ nanocomposite on monolayer graphene: From experiment to theory, J. Appl. Phys. 114 (2013) 204701-1–204701-12, with the permission of AIP Publishing].

was strongly related to the concentration of silver nanoparticles. Yang et al. [65] were first to study the photocatalytic and antimicrobial abilities of the low-cost, large-scale producible bifunctional TiO₂/Ag₃PO₄/graphene composites under visible light. Fabrication of three-phases composite result better dispersibility, which is a viable factor in governing the photocatalytic and antimicrobial effects. Each of the components plays a specific role in this bifunctional system. Firstly, the large surface area of reduced graphene form affects the improvement of the adsorption of organic compounds and enhances the absorption of visible light due to the black colour of the graphene sheet. Incorporation of Ag₃PO₄ in the structure of the composite favours absorption of visible light due to the suitable position of both valence and conduction band (CB 0.45 eV, VB 2.45 eV). Meanwhile, the photoexcited electrons of Ag₃PO₄ can be transferred through the conductive graphene matrix and further trapped by various oxygen groups present on the surface of graphene, thus successfully suppressing the recombination of photoexcited charge carriers and forming of ROS. These active species inactivate specific pathogens cells, while photogenerated holes of VB, transferred to the surface of Ag₃PO₄ and TiO₂ participate in the formation of highly reactive hydroxyl radicals for effective photocatalytic oxidation both microorganisms and organic pollutants in water. The mechanism of charge carrier transfer within the nanocomposite, as well as the results on photocatalytic inactivation of various pathogen cells, were presented in Fig. 4 [65].

Summarizing, the photoinactivation mechanism for graphene-based

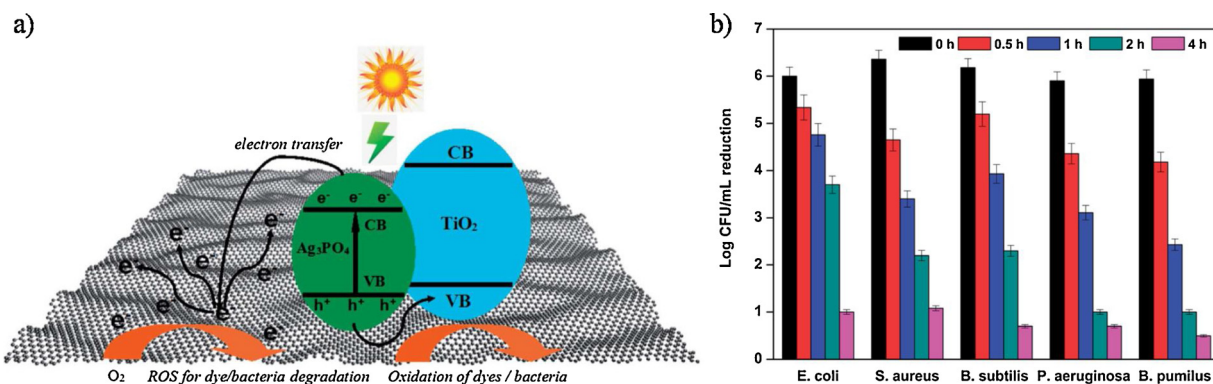


Fig. 4. Diagrams of a) the mechanism of photocatalytic degradation of organic dye molecules and bacteria under visible light irradiation, b) the time-kill analysis of the composite against different bacteria in the presence of $\text{TiO}_2/\text{Ag}_3\text{PO}_4/\text{GR}$ composite with 20 mg of GO and the molar ratio of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ of 0.8 [65, Reprinted by permission from Springer Nature: Springer, Journal of Materials Science: Materials in Electronics, Direct photo-oxidation and superoxide radical as major responsible for dye photodegradation mechanism promoted by TiO_2 -rGO heterostructure, G. Byzanski, D.P. Volanti, C. Ribeiro, V.R. Mastelaro, E. Longo, copyright 2018].

hybrids includes three main steps: bacterial cells adhesion/deposition on large-surface graphene sheets, membrane stress and disruptive interaction with bacteria, oxidizing a vital cellular structure or component. What is more, efficient separation of photogenerated charge carriers, the formation of a higher amount of ROS, the extended light absorption range in the case of solar light utilization, different metal and/or non-metal TiO_2 doping, the optimal reduction rate of GO as well as concentration of graphene in the nanocomposite, result in excellent inactivation rate of various pathogens in water.

4. TiO_2 /graphene nanomaterials for real urban wastewater treatment with further recommendations

The TiO_2 /graphene hybrid nanocomposites constitute a new group of nanomaterials which photocatalytic and antimicrobial performance is most frequently tested in laboratory conditions. Only a few works on the application of mentioned photocatalysts for real urban wastewater purification have been already published. Moreira et al. [68] compared different advanced oxidation systems with the usage of photo-Fenton, H_2O_2 reagents as well as TiO_2 P25 and GO-TiO_2 photocatalysis for solar-driven decomposition of organic micropollutants, human pathogen indicators, antibiotic-resistant bacteria and related genes in urban wastewater performed in a pilot-scale CPC photoreactor at Plataforma Solar de Almería (Spain). It was generally found that the P25/ H_2O_2 system showed the best compromise to remove both biological and chemical pollutants due to the high intensity of UV radiation in the natural light spectrum (all tests were performed on sunny days between June and August). However, the high photocatalytic activity of TiO_2 -GO hybrids was pointed out in the case of organic micropollutants removal (carbamazepine, sulfamethoxazole, diclofenac) was highlighted. The main conclusion of the suppression of charge carriers recombination (investigated in detail in our previous work [23]) was confirmed under real conditions. Interestingly, the addition of hydrogen peroxide to tested photocatalysts increased the photodecomposition efficiency of P25 but significantly decreased the performance of TiO_2 -GO system due to the H_2O_2 attack to the underlying C–C bonds in the superficial defect sites of GO. Inactivation of total or resistant populations of faecal coliforms and enterococci was the most efficient for H_2O_2 -assisted systems but heterogeneous photocatalysis without hydrogen peroxide also performed quite well (TiO_2 -GO was the most efficient photocatalyst).

Similar enhanced photocatalytic properties of TiO_2 -rGO for urban wastewater treatment was found by Karaolia et al. [69]. It was generally concluded tested hybrid nanocomposite effectively removed erythromycin and clarithromycin antibiotics from purified wastewater. The high removal rate of selected antibiotic resistance genes (ARGs) was found for *ampC* and *ecfX* abundance of *Pseudomonas aeruginosa*. The other tested ARGs: *sul1*, *ermB* and enterococci-specific 23S rRNA, were

found to be photocatalysts-persistent. The high total genomic DNA stability in treated wastewater and its resistance to photocatalytic treatment was also confirmed.

In general conclusion, the TiO_2 /graphene-based hybrids can service a wide range of functional nanomaterials for water and wastewater treatment due to the combination of photocatalytic properties of titanium dioxide and remarkably good electrochemical performance of graphene. On the basis of detailed results obtained in real urban wastewater treatment systems, it can be clearly stated that studied TiO_2 /graphene photocatalysts can be utilized in the field of efficient solar harvesting devices as well as antibacterial medical applications. Therefore, there is a need for additional studies on the use of nanomaterials in real-water and wastewater treatment systems.

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This Special Issue is dedicated to honor the retirement of Prof. César Pulgarin at the Swiss Federal Institute of Technology (EPFL, Switzerland), a key figure in the area of Catalytic Advanced Oxidation Processes.

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